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The Behavior of the Infrared Spectrum of
Carbon Monoxide Adsorbed at Platinum Electrodes
from Non-Aqueous Solvents

by

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The Behavior of the Infrared Spectra of
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From Non-Aqueous Solvents

Mark R. Anderson, Daniel Blackwood, and B. Stanley Pons

Abstract

.....

Carbon monoxide

Electrochemical oxidation of vanadium hexacarbonyl anion, $V(CO)_6^-$ in aprotic solvents results in formation of the $V(0)$ complex which decomposes to form CO in high concentrations next to the electrode surface. As a result, CO is more rapidly adsorbed on the surface than by conventional methods. Surface reflection infrared spectroscopy shows that the potential dependent frequency shift for the infrared active bands due to CO adsorbed on platinum is $19\text{ cm}^{-2}/V$ in 1,2-dichloroethane and $22\text{ cm}^{-2}/V$ in acetonitrile, which are considerably less than the $30\text{ cm}^{-2}/V$ observed in aqueous systems. (A-1)



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**The Behavior of the Infrared Spectrum of
Carbon Monoxide Adsorbed at Platinum Electrodes
From Non-Aqueous Solvents**

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Introduction

It has been shown that $V(CO)_6^-$ is readily oxidized electrochemically to the neutral species at a platinum electrode in noncoordinating, nonaqueous solvents (1). In the presence of competing complexing ligands (acetonitrile or water, for example) the neutral species will rapidly decompose to produce CO (1-3).

The behavior of the vibrational spectra of adsorbed CO at platinum electrodes has been studied extensively in aqueous systems (4-11). No studies, however, have been reported in the literature concerning the vibrational spectra of adsorbed CO in the presence of nonaqueous solvents. Studies utilizing different conditions, particularly solvent changes, would be beneficial in demonstrating the importance of the environment in the infrared spectrum of adsorbed CO. The reason for the nonexistence of studies of CO adsorption in the presence of aprotic solvents is perhaps the low solubility of CO in these aprotic solvents or the extensive surface cleaning, alternately growing and stripping of a platinum oxide adlayer, required in the aqueous systems which might not be easily accomplished in aprotic solvents.

By producing CO in situ via an uncomplicated electrochemical reaction, one can form a relatively high adsorbate concentration at the electrode surface which promotes adsorption. This paper describes a procedure using the electrochemical behavior of the $V(CO)_6^-$ species in the presence of competing ligands to produce CO in situ. With this preparation, the behavior of the infrared spectra of adsorbed CO formed in the presence of nonaqueous solvents are presented and discussed.

Experimental

Tetraethylammonium vanadiumhexacarbonyl (-I) was prepared and purified by standard procedures. The resulting yellow powder was found to be stable at room temperature for several days in the presence of atmospheric oxygen. Acetonitrile (Aldrich Gold Label) and 1,2-

dichloroethane (EM Scientific) were used as supplied. No attempt was made to remove nominal water present in the 1,2-dichloroethane (0.03%) in most experiments as we find the presence of water is required in the experiment to serve as the competing ligand in this solvent. When "dry" 1,2-dichloroethane was required in the study, 1,2-dichloroethane was stored over molecular sieves (MCB Manufacturing Chemists, Inc., type MX1583A-1) to remove the residual water. The "dryness" of the 1,2-dichloroethane was accessed by the reversibility of the oxidation of $V(CO)_6$. The dry 1,2-dichloroethane was filtered prior to being used in electrochemical experiments in order to remove residual particulates from the solvent. All supporting electrolytes were of analytical reagent grade, and were dried under vacuum before use. All glassware was cleaned in a 50:50 (V:V) mixture of HNO_3 and H_2SO_4 , rinsed with triply distilled water, steamed (triply distilled water) for half an hour, and dried in an oven at 35°C.

To reduce the amount of infrared radiation loss due to solvent absorption, a thin layer cell of the type previously described was used (12). The surface infrared spectra were obtained by difference reflection. The FTIR spectrometer was a vacuum bench Bruker/IBM Model IR/98.

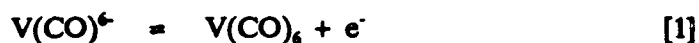
The platinum mirror working electrode was prepared by polishing the surface with successively finer grades of alumina, down to 0.05 micron. The electrode was then placed into the electrolyte, and the solution was deoxygenated for 20 minutes with argon. After deoxygenation, the electrode was cycled between -0.8V and 1.0V vs. SCE (the positive potential was not great enough to form the oxide) at 10mV/s in the positive direction and 3V/s in the negative scan direction for five minutes. The electrode was then pushed against the infrared transparent CaF_2 window to form the thin solution layer.

A saturated calomel reference electrode (SCE) was used as the potential reference in the 1,2-dichloroethane solution, while a Ag/Ag^+ reference electrode (approximately +0.20V vs. SCE) was used in the acetonitrile solutions. In the 1,2-dichloroethane solution the liquid junction potential between the nonaqueous solvent and the aqueous reference electrode, as determined from

the oxidation potential of ferrocene/ferrocinium couple, was found to be approximately 250mV. All potentials presented in this paper have been corrected for the liquid junction potential and converted to the SCE reference scale.

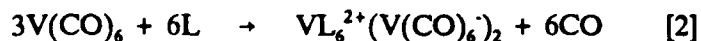
Results and Discussion

The redox potential for the reaction



in the presence of 0.10M tetrabutylammonium tetrafluoroborate/1,2-dichloroethane at a platinum electrode was determined from cyclic voltammetry to be approximately -0.1V vs. SCE (Figure 1). SNIFTIRS spectra in the presence of dry 1,2-dichloroethane showed that the infrared active vibrations in the anion occurred at 1855cm⁻¹ and 1900cm⁻¹ (shoulder), while the neutral species showed only one band at 1971cm⁻¹ (Figure 2).

In the presence of a competing ligand, such as water or acetonitrile, neutral V(CO)₆ readily undergoes a disproportionation reaction (reaction 2) to generate CO (1-3).



Evidence for this reaction is obtained in the difference spectrum of the V(CO)₆⁻/V(CO)₆ couple at potentials on opposite sides of the oxidation potential. If reaction 2 were to occur as expected, V(CO)₆ will be consumed and should not appear in the difference spectrum. In the spectrum (Figure 3a), the band attributable to V(CO)₆⁻ disappears (1855cm⁻¹) without the expected appearance of V(CO)₆ bands (1971cm⁻¹). Unfortunately, bands attributable to the VL₆ species were never identified to aid in the confirmation of reaction 2.

Figure 3b shows that the CO produced in reaction 2 is present in two forms: solution dissolved CO and adsorbed CO. Solution dissolved CO has an infrared band at 2135cm^{-1} . The position of this band is independent of electrode potential. If the chemical decomposition of the $\text{V}(\text{CO})_6$ occurs close to the electrode surface, the CO may also adsorb onto the platinum, producing a potential dependent infrared band at about 2075cm^{-1} (Figure 3b). The frequency of the latter band was found to shift by $19\text{cm}^{-1}/\text{V}$ as the electrode potential was altered (Figure 4 and Table 1). The CO peak intensity remained constant (within experimental error) until the onset of oxidation to CO_2 at about 1.0V vs. SCE. Other workers have reported the observation of an additional CO band under other experimental conditions at approximately 1850cm^{-1} corresponding to a bridge bonded species (4,8-11). In the current studies the bridge bonded species was not observed probably because of the overwhelming intensity of the CO stretch of $\text{V}(\text{CO})_6^-$ at nearly the same frequency.

The potential shift of the infrared active band due to CO adsorbed on platinum from aqueous electrolytes has previously been reported to be about $30\text{cm}^{-1}/\text{V}$. Both molecular orbital arguments (6,13) and electric field effects (the electrochemical Stark effect) (14-18) have been proposed to explain this phenomenon. A possible explanation for the significantly lower potential shift observed in 1,2-dichloroethane could be that the much lower permittivity of this solvent, bulk value = 10.3, compared with the permittivity of water, bulk value = 78, results in a less compact double layer in 1,2-dichloroethane giving rise to a smaller potential drop across the adsorbed CO molecules. Indeed, when 1,2-dichloroethane was replaced by a higher permittivity nonaqueous solvent, acetonitrile (bulk permittivity = 36), the rate of shift of frequency with potential was found to increase to $22\text{cm}^{-1}/\text{V}$. The dependence of the potential dependent frequency shift on the solvent permittivity is a subject that is under continued study and will be reported in the near future.

In addition to its effect on the magnitude of the frequency shift with potential, changing the solvent from 1,2-dichloroethane to acetonitrile also resulted in an approximately 40% drop in the

peak intensity of the bands and a 15cm^{-1} shift in the peak position at any given potential (Table 2). This is considered to be due to a decrease in the total coverage of the CO on the electrode surface due to the competition for adsorption sites with solvent molecules in the acetonitrile solution. Similar coverage effects have previously been reported for aqueous systems (19).

A coverage effect was also observed in 1,2-dichloroethane electrolyte when the amount of water in the solvent was reduced by storing over molecular sieves. Reduction in the water concentration had the effect of extending the lifetime of the neutral $\text{V}(\text{CO})_6$ species, as determined by cyclic voltammetry. The longer lifetime results in the diffusing of the neutral $\text{V}(\text{CO})_6$ away from the electrode surface before decomposing, and hence a lower concentration of CO near the surface. The spectrum in Figure 5 shows that in this case there are two low intensity potential dependent bands, one centered around 2075cm^{-1} and the other around 2020cm^{-1} . Infrared bands in similar positions have been reported previously in aqueous solutions (6) and have been assigned to two configurations of adsorbed linear bonded CO: a high and low coverage form, respectively. The peak intensity of the 2075cm^{-1} band increases with time at the expense of the intensity of the 2020cm^{-1} band, suggesting that the CO molecules migrate on the electrode surface to congregate in "islands".

Further evidence that CO competes with water or acetonitrile for adsorption sites on the platinum surface is shown in Table 3. In this Table, we report the effect on the spectra of changing the supporting electrolyte concentration. In 1,2-dichloroethane the main competition for adsorption sites will be between water and CO. There is also an equilibrium for water between free water and water involved in supporting electrolyte ion solvation. The distribution of water between surface adsorption and ion solvation is then expected to critically depend on the concentration of the supporting electrolyte. A reduction of the supporting electrolyte concentration is expected to result in an increase in the amount of adsorbed water and a corresponding decrease in the surface coverage of CO. This result is confirmed in Table 3.

The influence of the identity of the supporting electrolyte was also investigated. Table 4 shows that the supporting electrolyte identity has only a small effect upon the position and intensity of the CO infrared bands. The effect probably reflects coverage differences between the different solutions. As in the case of the different TBAF concentrations, the changes in the CO coverage is probably due to differences in the ability of the water in solution to solvate the various electrolytes.

It is interesting to note here that even with changes in the type and concentration of supporting electrolyte, the magnitude of the potential dependent frequency shifts always remains approximately $19\text{cm}^{-1}/\text{V}$ in 1,2-dichloroethane and $22\text{cm}^{-1}/\text{V}$ in acetonitrile. In addition, the CO band intensity remains relatively constant over the potential range investigated during any individual experiment. The last observation indicates that the surface coverage of CO remains constant during the course of an experiment. Consequently, the potential dependent band shifts may be ascribed to changes brought about by the electrode potential rather than by changes in the CO surface coverage.

Finally the effect of adding acetonitrile to dry 1,2-dichloroethane solutions was investigated (Table 5). In the dry 1,2-dichloroethane solvent, the added acetonitrile serves as the competing ligand in the disproportionation reaction of $\text{V}(\text{CO})_6$. Small additions of acetonitrile (0.006M total concentration) were found to produce a small amount of adsorbed CO. The low acetonitrile concentration was thought to be insufficient to decompose a significant amount of the neutral $\text{V}(\text{CO})_6$, as shown by the nearly reversible voltammetric behavior of this solution. Further, this low concentration of acetonitrile was thought to be was large enough to effectively compete with the small amounts of CO present for the adsorption sites. Larger amounts of acetonitrile (over 0.025M total concentration), however, were found to slightly increase the amount of CO adsorption relative to the 0.006M acetonitrile solution despite the increased amount of acetonitrile available for adsorption. Evidence for this conclusion is seen in the slightly larger peak intensity in the solutions

of higher acetonitrile concentration as well as the frequency shift of the CO bands to higher wavenumber. Higher acetonitrile concentrations are thought to decompose the $V(CO)_6$ species producing a much higher CO concentration near the electrode surface, resulting in more favorable competition for surface sites by CO.

Conclusions

An effective method of generating CO adsorbate molecules from nonaqueous solutions has been demonstrated. Attempts to obtain CO adsorption in the presence of aprotic solvents by the more conventional method of bubbling CO in the aprotic solvent were unsuccessful in this research. The inability of more conventional methods of obtaining CO adsorption in these solvents has probably prevented the study of this system previously.

It has been found that the potential dependent frequency shift of adsorbed CO in nonaqueous solutions ($19\text{cm}^{-1}/\text{V}$ in 1,2-dichloroethane and $22\text{cm}^{-1}/\text{V}$ in acetonitrile) is markedly less than in aqueous systems ($30\text{cm}^{-1}/\text{V}$), and it is proposed that this may be due to the lower permittivity of the nonaqueous solvents reducing the proportion of the potential gradient that falls across the adsorbed molecule. In addition, it has been found that the vibrational frequency of adsorbed CO in the solvents investigated at any given potential depends on the surface coverage as it does in aqueous solutions. The coverage, however, does not effect the magnitude of the potential dependent frequency shift.

ACKNOWLEDGEMENT

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Legends for the Figures

- Figure 1. Cyclic voltammogram of $0.001M (C_2H_5)_4N^+V(CO)_6^-$ in the presence of $0.10M$ tetrabutylammonium tetrafluoroborate/dry 1,2-dichloroethane at $100mV/sec$.
- Figure 2. SNIFTIRS spectrum of $V(CO)_6^-$ in the presence of dry 1,2-dichloroethane/ $0.10M$ tetrabutylammonium tetrafluoroborate. $E_{ref} = -0.40V$ vs. SCE, $E_{sweep} = 0.10V$ vs. SCE.
- Figure 3. SNIFTIRS spectrum of $V(CO)_6^-$ in the presence of $0.10M$ tetrabutylammonium tetrafluoroborate/1,2-dichloroethane. $E_{ref} = -0.40V$ vs. SCE, $E_{sweep} = 0.00V$ vs. SCE.
- Evidence for the decomposition of $V(CO)_6^-$, no band at $1971cm^{-1}$, and the production of CO, small band at $2075cm^{-1}$.
 - Expanded view of CO region, solution dissolved CO at $2135cm^{-1}$, linear bonded CO at $2075cm^{-1}$.
- Figure 4. SNIFTIRS spectrum of the linear bonded CO region as a function of applied electrode potential in the presence of $0.10M$ tetrabutylammonium tetrafluoroborate/1,2-dichloroethane.
- Figure 5. SNIFTIRS spectrum in the presence of $0.10M$ tetrabutylammonium tetrafluoroborate/1,2-dichloroethane of the linear bonded CO region for low coverage conditions: solution dissolved CO at $2135cm^{-1}$, high coverage linear bonded CO at $2079cm^{-1}$ - $2066cm^{-1}$, and low coverage linear bonded CO at $2027cm^{-1}$ - $2019cm^{-1}$. $E_{ref} = -0.20V$ vs. SCE, $E_{sweep} = 0.30V$ vs. SCE.

Table 1. Potential dependence of the infrared vibrational band for linearly bonded adsorbed CO as a function of electrode potential. Solution is 0.10M TBAF in 1,2-dichloroethane.

POTENTIAL (V vs. SCE)	BAND POSITION (cm ⁻¹)
-0.4	2069
-0.2	2073
0.1	2079
0.3	2083
0.5	2087

Table 2. Dependence of the infrared vibrational band for linearly bonded adsorbed CO on the solvent.

E V vs. SCE	SOLVENT 0.1M TBAF	BAND POSITION (cm ⁻¹)	PEAK INTENSITY $\Delta R/R$
0.50	1,2-EtCl ₂	2087	4.9×10^{-3}
	ACN	2073	2.8×10^{-3}
0.30	1,2-EtCl ₂	2083	4.9×10^{-3}
	ACN	2068	2.8×10^{-3}
0.10	1,2-EtCl ₂	2079	4.9×10^{-3}
	ACN	2064	2.8×10^{-3}
-0.20	1,2-EtCl ₂	2076	4.9×10^{-3}
	ACN	2057	2.8×10^{-3}

1,2-EtCl₂ is 1,2-dichloroethane

ACN is acetonitrile

TBAF is tetrabutylammonium tetrafluoroborate

Table 3. Dependence of the infrared vibrational band for linearly bonded adsorbed CO on Electrolyte concentration in 1,2-EtCl₂.

ELECTROLYTE	BAND POSITION (cm ⁻¹) at 0.3V vs. SCE	PEAK INTENSITY $\Delta R/R$
0.200M TBAF	2083	5.0×10^{-3}
0.100M TBAF	2083	4.9×10^{-3}
0.050M TBAF	2080	2.8×10^{-3}
0.025M TBAF	2078	1.3×10^{-3}

1,2-EtCl₂ is 1,2-dichloroethane
TBAF is tetrabutylammonium tetrafluoroborate

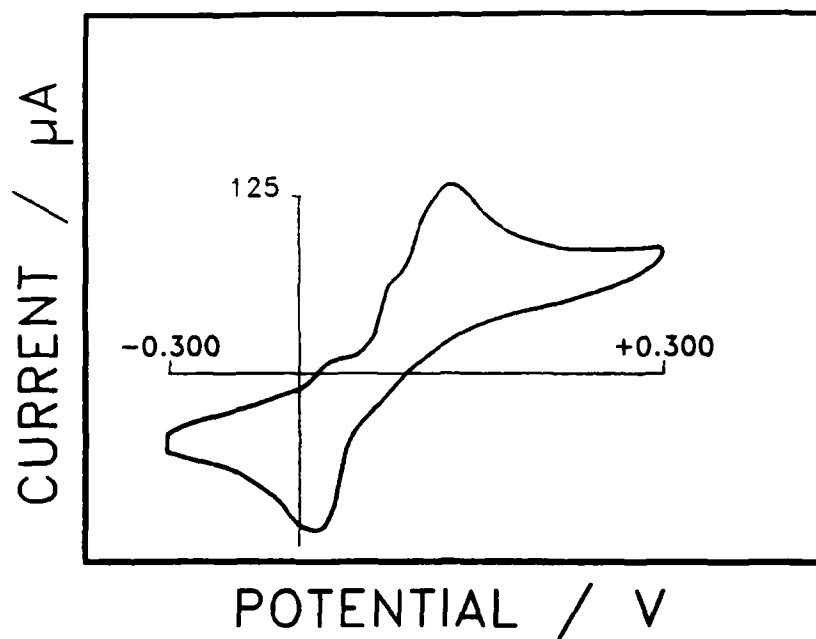
Table 4. Effect of Electrolyte identity on the vibrational band for linearly bonded CO.

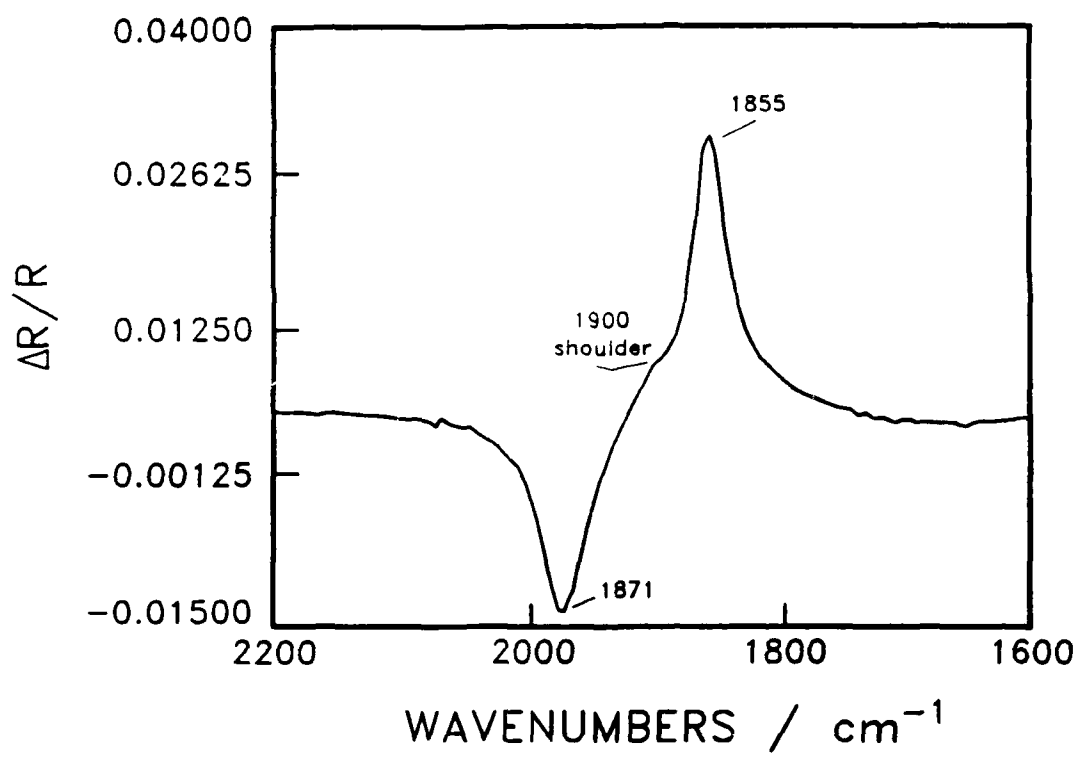
SOLUTION	BAND POSITION at 0.3V (cm ⁻¹)	PEAK INTENSITY $\Delta R/R$	RATE OF MOVEMENT cm ⁻¹ /V
0.1M TPAP in 1,2-EtCl ₂	2083	4.9×10^{-3}	19
0.1M TBAF in 1,2-EtCl ₂	2083	4.0×10^{-3}	19
0.1M TOAP in 1,2-EtCl ₂	2080	4.0×10^{-3}	18
0.1M TBAA in 1,2-EtCl ₂	2080	3.5×10^{-3}	19
0.05M TEAF in 1,2-EtCl ₂	2079	3.0×10^{-3}	17
0.05M TBAF in 1,2-EtCl ₂	2080	2.8×10^{-3}	19
0.025M TBAF in 1,2-EtCl ₂	2078	1.3×10^{-3}	19

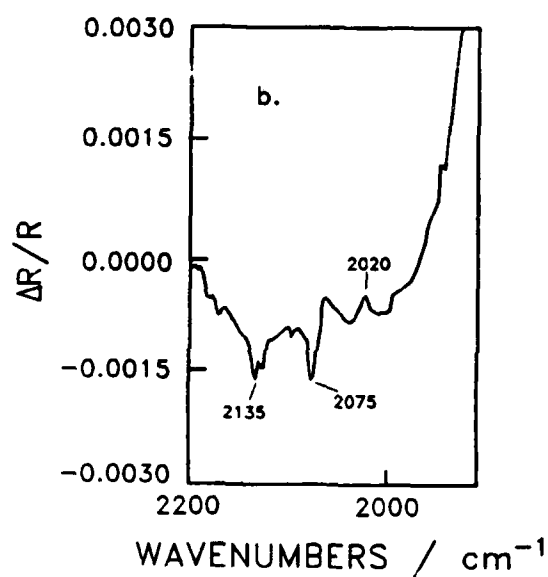
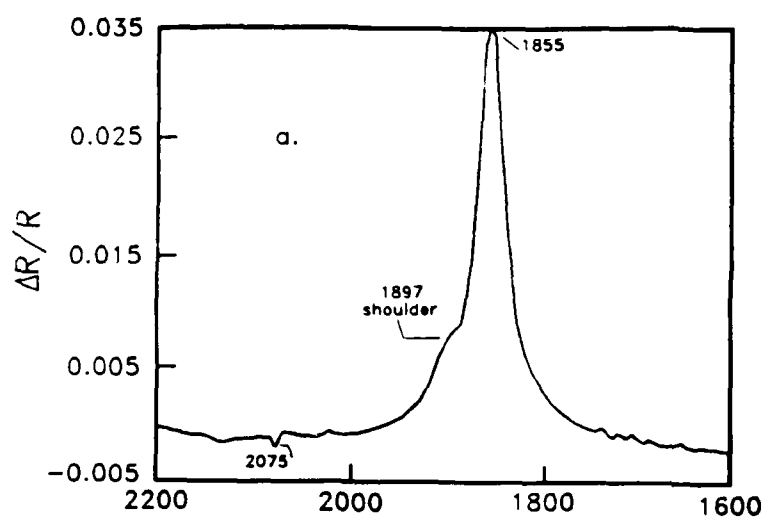
TPAP is tetrapropylammonium perchlorate
 TBAF is tetrabutylammonium tetrafluoroborate
 TOAP is tetraoctylammonium perchlorate
 TBAA is tetrabutylammonium acetate
 TEAF is tetraethylammonium tetrafluoroborate
 1,2-EtCl₂ is 1,2-dichloroethane

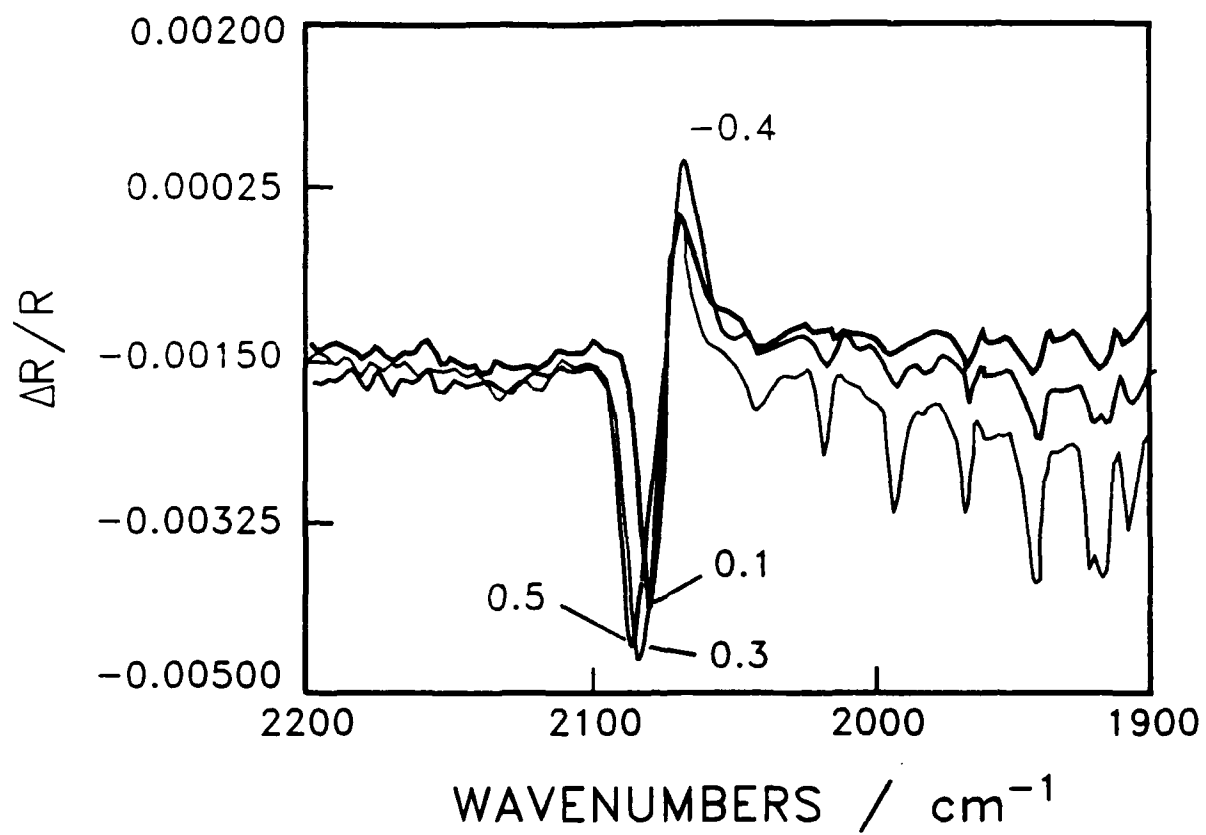
Table 5. Dependence of the infrared vibrational band for linearly bonded adsorbed CO on acetonitrile (ACN) concentration in 1,2-EtCl₂.

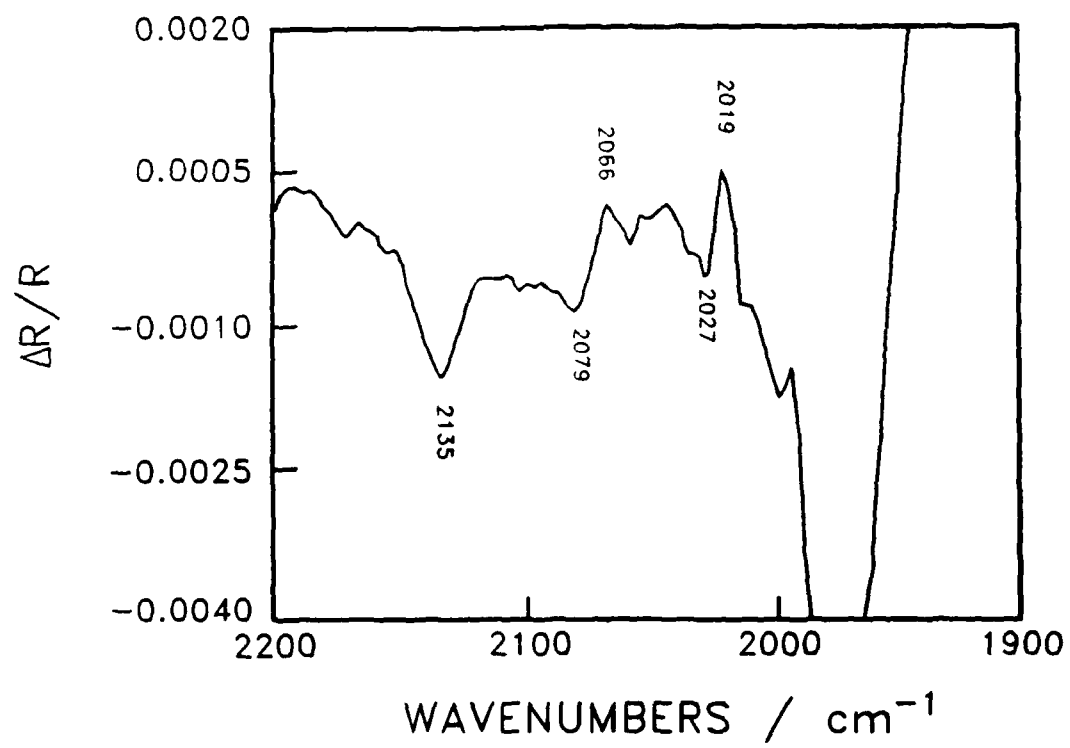
ACN CONCENTRATION millimolar	BAND POSITION (cm ⁻¹) AT +0.3V	PEAK INTENSITY $\Delta R/R$
0.0	No CO adsorption	
6.0	2075	2.0×10^{-3}
12.0	2077	2.3×10^{-3}
25.0	2078	2.3×10^{-3}
100.0	2080	2.3×10^{-3}
500.0	2080	2.3×10^{-3}











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